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Water–Surfactant Contact Studied by ^{19}F–^{1}H Heteronuclear Overhauser Effect Spectroscopy

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Intermolecular ^{19}F–^{1}H cross-relaxation is measured using heteronuclear Overhauser effect NMR spectroscopy (HOESY) in the micellar solution of cesium pentadecafluorooctanoate. The results are analyzed in terms of a weak ^{1}H–^{19}F cross-relaxation between the water protons and the fluorines in the fluoroalkyl chain and a strong ^{19}F–^{19}F cross-relaxation within the fluoroalkyl chain. The water–surfactant cross-relaxation indicates a water approach to the first CF_2 segment in the order of 2.0 Å and a short (≪ns) water residence time. Evidence of fluorine hydration further inside the micelle is presented.

Key Words: **cross relaxation; HOESY; surfactant; water; micelle.**

INTRODUCTION

The state of interface between surfactant aggregates and the solvent, which is most often water, has been the subject of extensive studies. Since the presence of water mediates the headgroup–headgroup interaction, the water in the headgroup region has profound importance for the phase behavior of surfactant systems. There are three main NMR approaches to this problem, two of which, based on measuring the self-diffusion and the spin relaxation of water, are the more traditional ones. The water diffusion method (*1–5*) uses the fact that the water in the interface region has a lower mobility than that in bulk water and that the water is (on the time scale of the experiment) in fast exchange between the interface and the bulk regions. Thus, the measured diffusion coefficient is the population average of the diffusion coefficients in those two regions. The water relaxation method (*6, 7*) is usually based on the quadrupolar relaxation of the water nuclei ^{2}H or ^{17}O and works under the same principle, with the important difference that the slower water dynamics in the interface region is detected via the increased relaxation rates. The dynamical (i.e., how much is the water motion reduced at the interface) and the population (i.e., how many water molecules hydrate the headgroups) information cannot be easily separated by either method.

The third NMR approach (*8–10*) observes the dipolar cross-relaxation (*11, 12*) between the water and the surfactant spins. Cross-relaxation NMR spectroscopy has been successfully applied to the hydration of biomolecules (*13, 14*) and tissues (*15–17*), but to date there have been only a few such studies in surfactant systems. Those experiments often detected the heteronuclear cross-relaxation between water protons and nuclei of some nonprotonated atoms, such as the ^{13}C in the carboxylate group of octanoate (*9, 10*) or the ^{31}P in the phosphate group of phosphatidylcholine (*8*), and provided information about the average water distance to those atoms.

Our study is motivated by two recent cross-relaxation experiments (*18, 19*), both of which seem to indicate long water residence times in the headgroup region. Such a claim (i.e., long water residence times in fully hydrated systems) contradicts a huge amount of earlier evidence from NMR relaxation (*6, 7*) as well as from neutron scattering (*20, 21*). Cross-relaxation is, however, a rather direct method for measuring the order of magnitude of the water residence time via the sign of the observed cross-relaxation rate; a negative rate indicates a long (≥ns) residence time while a positive rate implies a short (≪ns) residence time, and those two recent studies observed negative cross-relaxation rates (in form of positive NOESY cross-peaks) between water and headgroup protons. Since traditional tools could be classified as indirect in this instance, a finding with a ''direct'' method such as cross-relaxation (where the sign of the cross-relaxation rate provides a ''null experiment'') that contradicts common belief should not just be neglected. Therefore, we chose to present here some related results on a perfluorinated surfactant where, instead of ^{1}H–^{1}H NOESY, we look at the cross-relaxation between water protons and the ^{19}F nuclei in a perfluoroalkyl chain (we note that the ^{19}F–^{1}H HOESY experiment has already been applied to hydration studies of a fluorinated protein (*22*)). The ^{19}F and ^{1}H resonance frequencies are very close, and therefore the $\sigma(H\text{–}F) = 6J(\omega_H + \omega_F) - J(\omega_H - \omega_F)$ cross-relaxation rate (*11*) can become negative, just as a homonuclear ^{1}H–^{1}H cross-relaxation rate in the absence of extreme narrowing provided that the correlation time describing slow motion is of the order or larger than 10^{-9} s. On the other hand, the ^{1}H–^{19}F arrangement is convenient (as compared to ^{1}H–^{1}H experiments) as it makes simple to perform less time-consuming 1D cross-relaxation experiments.

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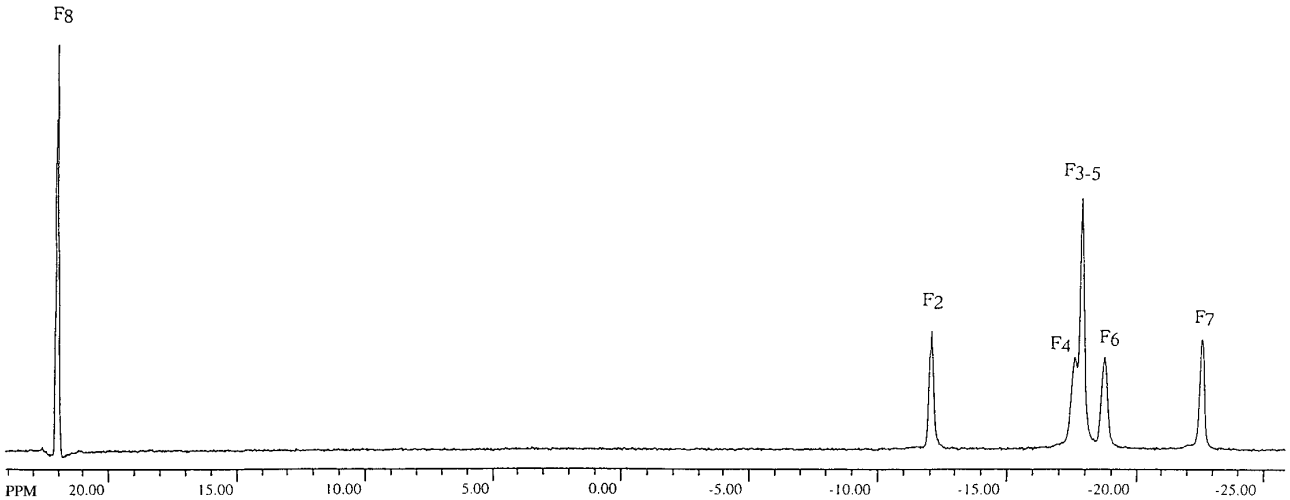

FIG. 1. The ^{19}F spectrum of the investigated CsPFO/water system. The assignment of the peaks determined by ^{19}F 2D COSY spectroscopy is also indicated.

EXPERIMENTAL

Cesium pentadecafluorooctanoate (CsPFO), prepared as described elsewhere (*23*), has been mixed with doubly distilled H_2O. The sample of neutral pH has 42.6 wt% surfactant which means that there are about 40 water molecules per surfactant. At 45°C, where the NMR measurements were performed, the sample is in the isotropic micellar phase (*24*). Correspondingly, the ^{19}F NMR spectrum, shown in Fig. 1, provides peaks without dipolar splittings.

All experiments involving the fluorine nucleus have been performed at 4.7 T using a homebuilt NMR spectrometer equipped with a homebuilt ^{13}C–^{2}H–^{19}F–^{1}H double-coil, quadruple-tuned probe. The longitudinal relaxation time of water ^{17}O has been measured with the same spectrometer and with a standard homebuilt broadband probe.

The ^{19}F spectrum has been assigned by a 2D COSY experiment (result not shown). In contrast to alkanes, the four-bond F–C–C–C–F *J*-couplings are usually larger than the three-bond F–C–C–F *J*-couplings (*25*), and therefore the most intense COSY cross-peaks are expected between fluorines in the second-nearest CF_2 groups. The assignment given in Fig. 1 is based on the profound F_2–F_4–F_6–F_8 and F_3–F_5–F_7 connectivities; the chain positions are numbered from the carboxylate carbon, and thus the first fluorine is F_2 and the last one is F_8. Since signals from F_3 and F_5 coincide, only the sum of their intensities ($F_{3–5}$) can evidently be considered.

Water ^{1}H and surfactant ^{19}F nonselective longitudinal relaxation times T_1 were measured by saturation-recovery, water ^{17}O T_1 by inversion recovery, and the carboxylate ^{13}C T_1 by the SUFIR method (*26*). Cross-relaxation between carboxylate ^{13}C and F_2 was estimated through the NOE factor by comparing carbon intensities under continuous and gated (during acquisition) decoupling conditions, respectively.

The pulse sequence for ^{19}F–^{1}H heteronuclear Overhauser effect (HOE) experiments, shown in Fig. 2, is derived from the one used earlier for ^{1}H–^{13}C 1D HOE experiments (*9*) by replacing the initial inversion by saturation in order to avoid any problems associated with radiation damping. The quality of the RF defocusing (''saturation'') pulses has been controlled by test experiments with a (π/2) pulse placed after the saturation pulse; the detected ^{19}F signal was less than 30% of the smallest cross-relaxation peaks. The ^{19}F peak intensities recorded at different mixing times t_m and relative to the single-pulse ^{19}F reference spectrum with the same number of scans are shown in Fig. 3; significant cross-relaxation responses are observed for F_2–F_7. It can be noticed that F_3–F_7 curves are virtually identical, indicating efficient spin diffusion along this fluorine spin system. Attempts to measure ^{1}H–^{13}C cross-relaxation were carried out by a similar method with additional fluorine decoupling during acquisition. Since the significant signal overlap (F_3–F_5) and the strong spin diffusion (see below) render a 2D NOESY experiment excessive and less helpful in elucidating ^{19}F–^{19}F cross-relaxation, we therefore decided to rely on a 1D experiment that consists of selectively

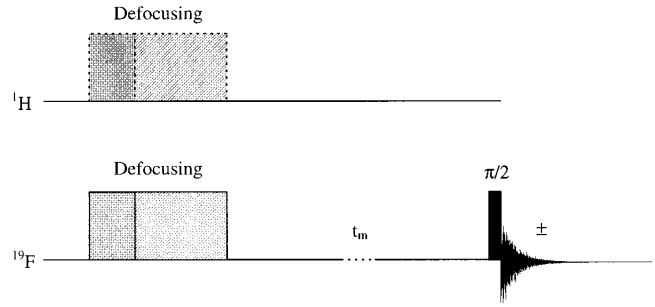

FIG. 2. The pulse sequence used for 1D ^{1}H–^{19}F HOE experiments. Defocusing (saturation) schemes consist of two long pulses with different phases, typically $(4\ \text{ms})_x(8\ \text{ms})_y$. ^{1}H saturation is applied in every other scan.

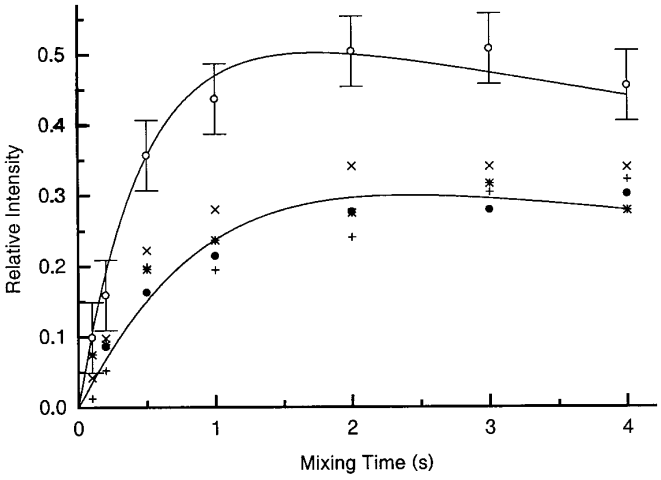

FIG. 3. The observed HOE (by the experiment in Fig. 2) peak intensities in percent units (relative to those in a 90°-pulse spectrum of equivalent number of scans) determined at different mixing times for F_2 (○), F_{3-5} (×), F_4 (*), F_6 (+), and F_7 (●). For each mixing time, 4000 transients were accumulated with a recycle time of 20 s. The solid lines are the results of the fits as described in the text. The experimental error, given for the F_2 intensities, is about the same for the other peaks as well.

saturating F_2 and monitoring thereafter (i) the recovery of F_2 and (ii) the time course of all other signals which are rather similar to each other. Selective saturation was achieved by the DEBOG sequence (*27*), and a typical result is shown in Fig. 4.

RESULTS AND DISCUSSION

The first piece of information that is required for the analysis of the cross-relaxation data is the number of water molecules that are found in the headgroup region of the surfactant (''bound water''). In dilute micellar phases, this quantity has often been estimated by directly comparing the self-diffusion coefficient of water in the micellar sample to its bulk value (*1–5*). In the present dense (almost 30% volume fraction) micellar system, this strategy cannot be followed since obstruction effects significantly reduce the long-range translational diffusion coefficient (*23*); thorough analysis of the water diffusion and quadrupolar splitting data in the nearby nematic phase of the same system yielded the most plausible number of water molecules per headgroup as about 6 (*23*). We assume the same number of ''bound'' water molecules in the micellar phase.

As has been amply demonstrated earlier (*1–7*), the dynamics of the water molecules associated with the headgroup region is slowed down as compared to that in bulk water. The analysis of the diffusion data cited above has also indicated that the diffusion coefficient of the water molecules in the headgroup region is 2–3 times lower than the bulk value. In our analysis (see below) we shall assume that the dominant dynamical mode to cause the observed cross-relaxation is the tumbling of water molecules in the bound state for which the correlation time can be evaluated by comparing the ^{17}O relaxation rates (Table 1) in the micellar sample and in bulk. Assuming $N = 6$ ''bound'' water molecules, we obtain a correlation time τ_c of about 4.5 ps, which is about 2.5 times the value found in bulk water at 45°C (*7*, *28*).

Next, the constraints of the analysis that are imposed on us by the particular structural features and relaxation behavior of the system have to be investigated. The recovery of the F_2 signal in the selective ^{19}F saturation (on F_2) experiment showed the selective longitudinal relaxation rate of F_2 to be about 2.5 times larger (Table 1) than the nonselective longitudinal relaxation rate of the same nucleus. This fact, together with the observed weak variation of the nonselective R_1^F, clearly indicates that the spin diffusion is rapid along the alkyl chain (*11*). In other words, a (weak) selective perturbation of the equilibrium magnetization effects the chain homogeneously on the $\leq$1 s timescale. Second, because of the larger C–F bond length (*29*), the all-trans (for the carbons) distance between second-neighbor (e.g., between F_2 and F_4) fluorines is smaller than the all-trans distance between next-neighbor fluorines (F_2 and F_3). Therefore, the cross-relaxation between second-neighbor fluorines could not be neglected (as perhaps in protonated chains (*30*)) in a detailed analysis. These two points, together with the F_3–F_5 spectral overlap, indicate that the relaxation behavior of the F_{3-7} fluorines cannot be treated separately. On the positive side, it is then a good approximation to represent these fluorines as a single pool of longitudinal magnetization. Within this model it is straightforward to analyze the recovery curves of the F_{3-7} peaks (see Fig. 4 for a typical spectrum) in the selective ^{19}F saturation experiment; from the initial behavior of the relevant evolution curves we derived an estimate for $\sigma_{F_2-F_{3-7}}$ (see Table 1). As also indicated by the sign of the F_{3-7} peaks in Fig. 4, this cross-relaxation rate is negative, which again shows that the zero-frequency spectral density, included in the relaxation rates, is large and therefore the spin diffusion along the chain is rapid.

Within this approximation we can quantitatively analyze the cross-relaxation data in Fig. 4. Since one can anticipate that the water–surfactant ^1H–^{19}F cross-relaxation rate is much smaller than $\sigma_{F_2-F_{3-7}}$, the short-time expansion of the relaxation matrix (*30*) is less suitable for describing the qualitative features of the experimental data. Therefore, we fitted the relaxation data to the full solution of the following extended Solomon equation (*31*):

$$\begin{aligned}
\frac{d}{dt} I_z^H &= -R_1^H(I_z^H - 12I_{eq}^H) - 12\sigma_{HF_2}(I_z^{F_2} - 2I_{eq}^F) \\
&\quad - 12\sigma_{HF_{3-7}}(I_z^{F_{3-7}} - 10I_{eq}^F) \\
\frac{d}{dt} I_z^{F_2} &= -R_1^{F_2}(I_z^{F_2} - 2I_{eq}^F) - 2\sigma_{HF_2}(I_z^H - 12I_{eq}^H) \\
&\quad - 2\sigma_{F_2F_{3-7}}(I_z^{F_{3-7}} - 10I_{eq}^F) \\
\frac{d}{dt} I_z^{F_{3-7}} &= -R_1^{F_{3-7}}(I_z^{F_{3-7}} - 10I_{eq}^F) - 10\sigma_{HF_2}(I_z^H - 12I_{eq}^H) \\
&\quad - 10\sigma_{F_2F_{3-7}}(I_z^{F_2} - 2I_{eq}^F). \qquad [1]
\end{aligned}$$

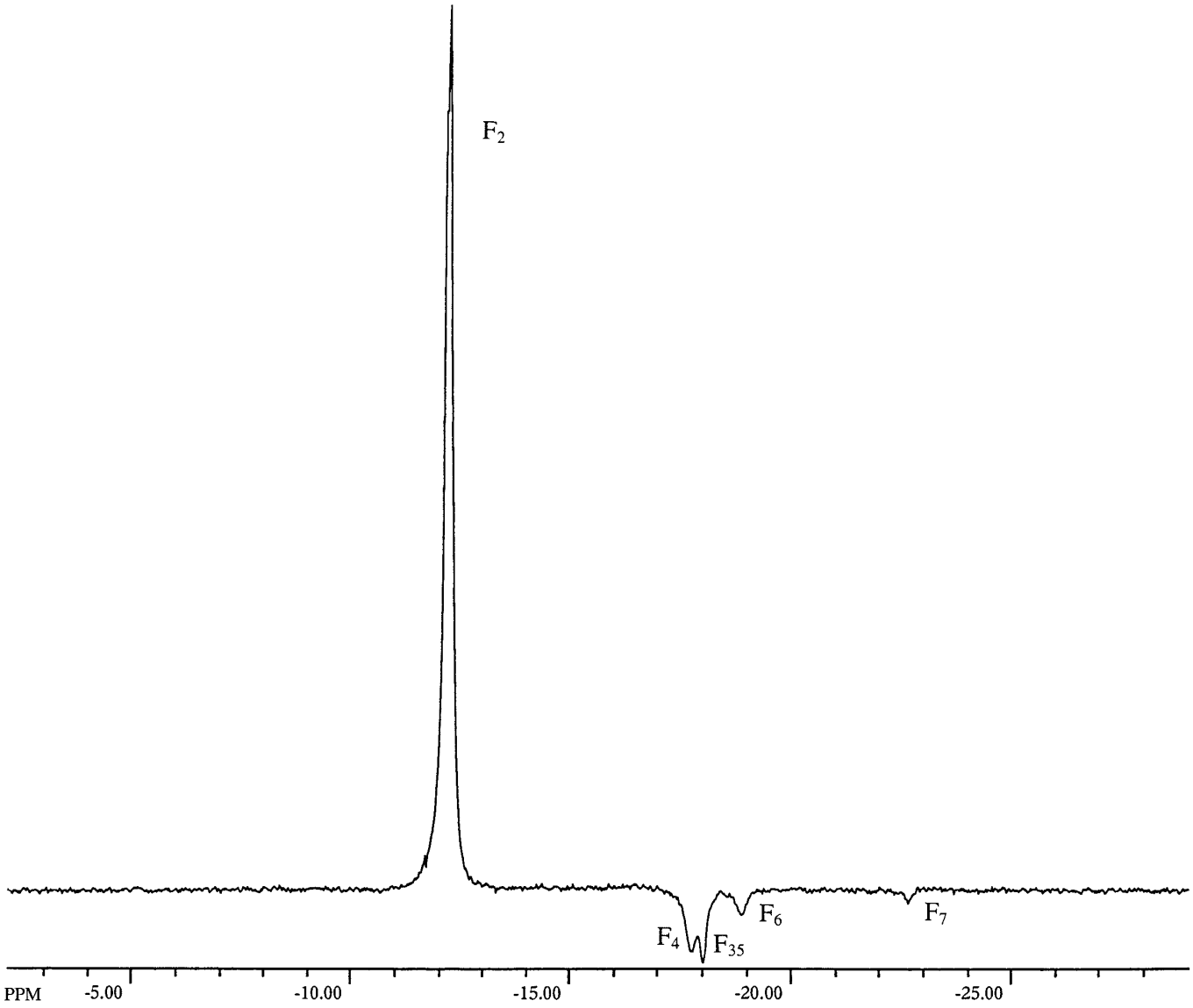

FIG. 4. The ^{19}F spectrum obtained by subtraction (*9*) of the following two experiments: [F_2 selective saturation] − Acquisition; [F_2 selective saturation] − t_m − Acquisition with t_m = 500 ms.

In this equation, I_{eq}^{H} and I_{eq}^{F} represent the equilibrium magnetization of one proton and one fluorine, respectively, whereas any cross-relaxation rate σ is considered to involve only a single pair of nuclei. The longitudinal magnetizations are considered for all spins in the three respective groups; the number of spins in each group are accounted for in Eq. [1] by the appropriate coefficients in each term (*31*). From the experimental data, R_1^H, σ_{HF_2}, and $\sigma_{HF_{3-7}}$ were adjusted (the results are collected in Table 1) in the fitting procedure, while $\sigma_{F_2F_{3-7}}$ and $R_1^{F_2}$ were fixed to the values derived from the fluorine experiment with selective saturation. $R_1^{F_{3-7}}$, which anyway has only minor influence, was set to an estimated value slightly smaller than $R_1^{F_2}$. This last point means that no error is given in Table 1; we estimate that experimental uncertainty (see Fig. 3) results in an error of about 10% (or less) in the obtained cross-relaxation rates.

One important finding is the positive sign of the cross-relaxation rate $\sigma_{HF_2} = [6J(\omega_H + \omega_F) - J(\omega_H - \omega_F)]$, which indicates extreme narrowing and, thus, a short ($\ll$ns) residence time for the interfacial water. The two recent studies (*18*, *19*) that found negative cross-relaxation rates between water and surfactant or lipid headgroup protons were performed in systems where exchangeable protons (hydroxyl and amine) exist in the headgroups. Most probably, those exchangeable and indeed fast-exchanging protons (instead of protons belonging to water molecules hydrating the headgroups) are the source of the observed large and negative cross-relaxation rate of those studies.

TABLE 1
Longitudinal Relaxation Parameters (s^{-1})

	$R_1(H_2^{17}\underline{O})$	$R_1(\underline{H_2}O)$	$R_1(^{13}C)$	$R_1(^{19}F)$	$\sigma_{\underline{H_2}O-^{19}F}$	$\sigma_{\underline{F_2}-^{19}F,^{13}C}$
Sample (total)	101[a]	0.24[a]				
Sample (bound)		0.08[b]				
Pure water	65[a]					
Carboxylate			0.067[a]			0.144[a]
F_2 nonselective				0.92[a]		
F_2 selective				2.22[a]		
F_{3-5} nonselective				0.99[a]		
F_6 nonselective				0.92[a]		
F_7 nonselective				0.85[a]		
F_2					$1.9\ 10^{-3}$ [b]	
F_{3-7}					$7.1\ 10^{-4}$ [b]	$-3.9\ 10^{-2}$ [a]

[a] Directly measured.
[b] Extracted from the fit of data sets to Eq. [1] (see text).

The magnitude of the cross-relaxation rate between the water and the first segment of the fluoroalkyl chain of the surfactant molecule is in agreement with the findings of previous experiments (*8–10*). (Those studies probed heteronuclei such as ^{13}C and ^{31}P, which means that the sign of the obtained cross-relaxation rate between headgroup and water spins was not informative about the water residence time because of the small difference between the $J(\omega_H - \omega_X)$ and $J(\omega_H + \omega_X)$ spectral densities, where ω_H and ω_X are proton and heteronuclear angular frequencies, respectively.) Now we can tentatively express σ_{HF_2} as a function of a dynamical average distance r (*9*) and of the ''bound'' water rotational correlation time ($\tau_c = 4.5$ ps) as

$$\sigma_{HF_2} = \frac{1}{2}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{(\gamma_H \gamma_F \hbar)^2}{r^6}\,\tau_c, \qquad [2]$$

where the various symbols have their usual meaning. Using the experimental value of σ_{HF_2} given in Table 1, we obtain 2.0 Å for r. However, this result must be considered with some caution for the following reasons: (i) we assume that only rotational motions contribute to intramolecular cross-relaxation; (ii) we retain the water correlation time, derived in a rather indirect way; and (iii) we consider a homogeneous pool of water, with the protons in each molecule supposedly at the same distance to the fluorines in the CF_2 group. (On the other hand, because of the large power of r in Eq. [2], the distance parameter is rather forgiving to errors; a factor 2 change in τ_c leads to a mere 12% error in r. In any case, a 5×10^{-10} m^2/s translational diffusion coefficient for the ''bound'' water molecules provides about 20 ps average time for changing the H–F separation by 1 Å; this rough estimate indicates that it is reasonable to assume rotational motions to dominate the cross-relaxation.) The obtained value for R_1^H, which is obviously far too small, is probably a fitting artifact; this parameter is in strong covariance with the fixed $\sigma_{F_2F_{3-7}}$ and $R_1^{F_2}$.

Since the fluorines farther away from the micellar surface had to be grouped together during the analysis, information about water approach to those individual fluoromethylene groups is not available. There are two important points to make, however, from the obtained value of $\sigma_{HF_{3-7}}$. First, there is clearly a significant cross-relaxation between water and fluorines farther down on the fluoroalkyl chain. In other words, more than one fluoromethylene group is in contact with water, for which previously there has only been indirect evidence (*7, 32*). Secondly, the obtained value for $\sigma_{HF_{3-7}}$ cannot be smaller than the real value for σ_{HF_3}. This, under the assumption of identical water approach, provides a $N \leq 2$ upper limit for the water coordination of the second fluoromethylene group.

One should note that a frequently cited experiment (*33*) on the water penetration in micelles has already aimed at the intermolecular water–fluorine relaxation. In that study a 0.04 s^{-1} difference (with a precision in the same order) between the ^{19}F relaxation rates of F_2 in sodium pentadecafluorooctanoate micelles in H_2O and D_2O has been observed and ascribed to the intermolecular relaxation contribution from water. Because of the detection mode (i.e., the measurement of a small difference of two large quantities), no effect was found on the other fluorines in the fluoroalkyl chain; this should compare to our results.

Additional information about the arrangement of water molecules could be obtained from the cross-relaxation rate between the water protons and the carboxylate ^{13}C nucleus. The longitudinal relaxation rate and the cross-relaxation rate to F2 were readily available for the carboxylate carbon (see Table 1). However, numerous attempts (by a similar experimental procedure as for proton–fluorine cross-relaxation, but with additional fluorine decoupling during the acquisition) to detect proton–carbon cross-relaxation were totally fruitless. Nevertheless, taking into account the signal-to-noise ratio of a reference experiment and with the help of all other relaxation parameters, we were able to estimate an upper limit for σ_{HC},

which is about 4×10^{-4} s^{-1}. This corresponds to a $\geq$1.8 Å distance between water protons and the carboxylate carbon, which is not inconsistant either with the fluorine results or with results obtained in protonated analogues (*9*).

CONCLUSION

Because of the large chemical shift range and the large magnetogyric ratio of ^{19}F, ^{1}H–^{19}F cross-relaxation studies between water protons and surfactant fluorines are potentially helpful in elucidating water contact with amphiphile molecules. As shown above, some particular features of ^{19}F–^{19}F cross-relaxation within the fluoroalkyl chain only allowed an analysis of the experimental data in terms of a crude model, which, however, still provided us with the water–surfactant cross-relaxation rate ascribed to the first CF_2 segment. The small and positive cross-relaxation rate clearly provides, in agreement with overwhelming previous evidence (*6, 7*) and in contrast to some recent findings (*18, 19*), a short water residence time in the headgroup region of this surfactant. The obtained distance between water protons and the first CF_2 segment is rather small, indicating strong water penetration to the depth of the first alkyl chain. Similarly to indirect evidence in hydrogenated homologous systems (*7, 32*), we also obtain clear indication of nonnegligible hydration of fluorines farther inside the micelle.

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REFERENCES

1. B. Lindman and B. Brun, *J. Colloid Interface Sci.* **42,** 388 (1973).
2. N. Kamenka, B. Lindman, and B. Brun, *Colloid Polymer Sci.* **252,** 144 (1974).
3. W. Brown, R. Johnson, P. Stilbs, and B. Lindman, *J. Phys. Chem.* **87,** 4548 (1983).
4. P. G. Nilsson and B. Lindman, *J. Phys. Chem.* **87,** 4756 (1983).
5. P. G. Nilsson, H. Wennerström, and B. Lindman, *Chemica Scripta* **25,** 67 (1985).
6. B. Halle and H. Wennerström, *J. Chem. Phys.* **75,** 1928 (1981).
7. B. Halle and G. Carlström, *J. Phys. Chem.* **85,** 2142 (1981).
8. M. P. Milburn and K. R. Jeffrey, *Biophys. J.* **58,** 187 (1990).
9. D. Canet, N. Mahieu, and P. Tekely, *J. Am. Chem. Soc.* **114,** 6190 (1992).
10. M. Mahieu, P. Tekely, and D. Canet, *J. Phys. Chem.* **97,** 2764 (1993).
11. D. Neuhaus and M. Williamson, ''The Nuclear Overhauser Effect in Structural and Conformational Analysis,'' VCH, New York (1989).
12. H. Mo and T. C. Pochapsky, *Prog. NMR Spectrosc.* **30,** 1 (1996).
13. G. Otting, E. Liepinsh, and K. Wütrich, *Science* **254,** 974 (1991).
14. G. Otting and E. Liepinsh, *Acc. Chem. Res.* **28,** 171 (1995).
15. R. S. Balaban, *in* ''Encyclopedia of Nuclear Magnetic Resonance'' (D. M. Grant and R. K. Harris, Eds.), p. 2962, Wiley, Chichester (1996).
16. C. J. Baudouin, *in* ''Encyclopedia of Nuclear Magnetic Resonance'' (D. M. Grant and R. K. Harris, Eds.), p. 2946, Wiley, Chichester (1996).
17. R. G. Bryant, *in* ''Encyclopedia of Nuclear Magnetic Resonance'' (D. M. Grant and R. K. Harris, Eds.), p. 2954, Wiley, Chichester (1996).
18. F. Volke and A. Pampel, *Biophys. J.* **68,** 1960 (1995).
19. Z. J. Chen, L. C. M. VanGorkom, R. M. Epand, and R. E. Stark, *Biophys. J.* **70,** 1412 (1996).
20. A. C. Barnes, T. W. N. Bieze, J. E. Enderby, and J. C. Leyte, *J. Phys. Chem.* **98,** 11527 (1994).
21. S. König, E. Sackmann, D. Richter, R. Zorn, C. Carlile, and T. M. Bayerl, *J. Chem. Phys.* **100,** 3307 (1994).
22. D. P. Cistola and K. B. Hall, *J. Biomol. NMR* **5,** 415 (1995).
23. H. Jóhannesson, I. Furó, and B. Halle, *Phys. Rev.* **E53,** 4904 (1996).
24. N. Boden, K. W. Jolley, and M. H. Smith, *J. Phys. Chem.* **97,** 7678 (1993).
25. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, ''High Resolution Nuclear Magnetic Resonance Spectroscopy,'' Pergamon Press, Oxford (1965).
26. D. Canet, J. Brondeau, and K. Elbayed, *J. Magn. Reson.* **77,** 483 (1988).
27. D. Canet, J. Brondeau, E. Mischler, and F. Humbert, *J. Magn. Reson. A* **105,** 239 (1993).
28. J. C. Hindman, *J. Chem. Phys.* **60,** 4488 (1974).
29. A. M. James and M. P. Lord, ''Macmillan's Chemical and Physical Data,'' Macmillan Press, London (1992).
30. P. Palmas, P. Tekely, P. Mutzenhardt, and D. Canet, *J. Chem. Phys.* **99,** 4775 (1993).
31. D. Canet, H. Python, D. Grandclaude, and P. Mutzenhardt, *J. Magn. Reson. A* **122,** 204 (1996).
32. G. E. A. Aniansson, *J. Phys. Chem.* **82,** 2805 (1978).
33. J. Ulmius and B. Lindman, *J. Phys. Chem.* **85,** 4131 (1981).